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Kinetic Study on S_NAr Reactions of 1-(Y-substituted phenoxy)-2,4-dinitrobenzenes with Azide Ion: Effect of Changing Nucleophile from Hydroxide to Azide Ion on Reaction Mechanism and Reactivity

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Abstract

Second-order rate constants ($k_{\text{N}_3\text{Ar}}$) for $\text{S}_{\text{N}}\text{Ar}$ reactions of 1-(*Y*-substituted phenoxy)-2,4-dinitrobenzenes (**2a–2h**) with in 80 mol % H_2O /20 mol % DMSO at $25.0 \pm 0.1^\circ\text{C}$ have been measured spectrophotometrically. The $\log k_{\text{N}_3\text{Ar}}$ vs σ_{Y} plot is linear with $\rho = -0.38$. The Hammett plots correlated with σ_{Y} constants exhibit highly scattered points. In contrast, the Yukawa-Tsuno plot results in an excellent linear correlation with $\rho_{\text{Y}} = 1.02$ and $r = 0.51$, indicating that a negative charge develops partially on the O atom of the leaving *Y*-substituted phenoxy moiety in the transition state. Accordingly, the reactions have been concluded to proceed through a stepwise mechanism, in which expulsion of the leaving group occurs in the rate-determining step. Comparison of $k_{\text{N}_3\text{Ar}}$ with the k_{OHAr} values reported previously for the corresponding reactions with OH^- has revealed that is only 6- to 26-fold less reactive than OH^- toward substrates **2a–2h**, although the former is over 11 $\text{p}K_{\text{a}}$ units less basic than the latter. Solvation and polarizability effects have been suggested to be responsible for the unusual reactivity shown by and OH^- . Effects of changing nucleophile from OH^- to on reaction mechanism and reactivity are discussed in detail.

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